Fluorescence Spectroscopy

Excitation Profile

Raleigh light scattering

Light detected at 90°

Fluorescence emission

Exciting Wavelength Distribution

λ (nm)

λ (nm)
Scattering - TWO particle

Thomas Young - Royal Society, 1803
Scattering - MANY particles

10 nm

Many uniformly spaced sin waves

Constructive & Destructive Interference

Diffraction Pattern

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Scattering - MANY particles

Many pairwise groups of constructive & destructive interferences

But no coherent additivity

Constructive & Destructive Interference

Scattering but no pattern

Thomas Young - Royal Society, 1803

10 nm

450 nm
Dynamic Light Scattering

Pair of molecules yields scattering at a specific angle and magnitude

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering

Pair of molecules yields scattering at a specific angle and magnitude

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering

Pair of molecules yields scattering at a specific angle and magnitude

Different sizes - a new angle & magnitude

Constructive & Destructive Interference

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Dynamic Light Scattering
Photon Correlation Spectroscopy

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Volume empty - no scattering

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Volume empty - no scattering

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Smaller molecule scattering - angle 1

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Volume empty - no scattering

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Larger molecule scattering - angle 2

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Phonon Correlation Spectroscopy

Larger molecule scattering - angle 2

Constructive & Destructive Interference

10 nm

450 nm

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

Volume empty - no scattering

Constructive & Destructive Interference

Thomas Young - Royal Society, 1803
Dynamic Light Scattering
Photon Correlation Spectroscopy

\[ g^2(q,t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

\[ \langle f(t) \rangle = \text{time average of } f(t) \]
Dynamic Light Scattering
Photon Correlation Spectroscopy

Autocorrelation function

\[ g^2(q, t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

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Dynamic Light Scattering

Photon Correlation Spectroscopy

\[ g^2(q,t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

Autocorrelation function

Specific wave vector

\( \langle f(t) \rangle = \text{time average of } f(t) \)
Dynamic Light Scattering
Photon Correlation Spectroscopy

$$g^2(q,t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2}$$

Autocorrelation function

Specific wave vector

Time

$$\langle f(t) \rangle = \text{time average of } f(t)$$
Dynamic Light Scattering
Photon Correlation Spectroscopy

\[ g^2(q, t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

Autocorrelation function

Specific wave vector
time
Intensity of scattered light

\[ \langle f(t) \rangle = \text{time average of } f(t) \]
Dynamic Light Scattering
Photon Correlation Spectroscopy

Autocorrelation function

\[ g^2(q,t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

Small time interval

Specific wave vector

Time

Intensity of scattered light

\[ \langle f(t) \rangle = \text{time average of } f(t) \]
Dynamic Light Scattering
Photon Correlation Spectroscopy

\[ g^2(q, t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2} \]

Small time interval

Non-zero only when particles “stick around” in time \( \tau \)

Autocorrelation function

Specific wave vector

Intensity of scattered light

\[ \langle f(t) \rangle = \text{time average of } f(t) \]
Dynamic Light Scattering

Photon Correlation Spectroscopy

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non-zero only when particles “stick around” in time \( \tau \)

Relates to probability distribution function

\[ P(r,t | 0,0) = (4\pi Dt)^{-\frac{3}{2}} e^{-\frac{r^2}{4Dt}} \]
Dynamic Light Scattering
Photon Correlation Spectroscopy

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Relates to probability distribution function

\[ P(r,t | 0,0) = (4\pi Dt)^{-\frac{3}{2}} e^{-\frac{r^2}{4Dt}} \]

Assumes random (Brownian) motion
Dynamic Light Scattering
Photon Correlation Spectroscopy

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non-zero only when particles “stick around” in time \( \tau \)

Diffusion relates to size

\[ D = \frac{kT}{6\pi \eta R} \]
Dynamic Light Scattering
Photon Correlation Spectroscopy

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Diffusion relates to size

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Assumes spherical particles of radius \( R \)
Dynamic Light Scattering
Photon Correlation Spectroscopy

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non-zero only when particles “stick around” in time \( \tau \)

Diffusion relates to size

\[ D = \frac{kT}{6\pi \eta R} \]

Assumes spherical particles of radius \( R \)
Calibrate with particles of known size
Dynamic Light Scattering
Photon Correlation Spectroscopy

$$g^2(q,t) = \frac{\langle I(t) \cdot I(t + \tau) \rangle}{\langle I(t) \rangle^2}$$
Dynamic Light Scattering

Assumptions and Caveats

\[ D = \frac{kT}{6\pi \eta R} \]

Assumes

- Brownian motion
  - ★ non-interacting billiard balls
- Spherical scatterers
- Proper calibration for viscosity, etc
- Properly dilute solution
- No interference from other scatterers
Magnetic Resonance

Electron/Nuclear Magnetic Moment

Nuclei

$$\vec{\mu}_m = \frac{g_n \beta_n}{\hbar} \vec{L} = \gamma_n \vec{L}$$

$$\beta_n = 5.05 \times 10^{-24} \text{ erg} \cdot \text{ gauss}^{-1}$$

$$\gamma_{n/e} = \text{gyromagnetic ratio}$$

Bohr magneton

$$\beta_e = 9.27 \times 10^{-21} \text{ erg} \cdot \text{ gauss}^{-1}$$

Electrons

$$\vec{\mu}_m = \frac{g_e \beta_e}{\hbar} \vec{L} = \gamma_e \vec{L}$$
Magnetic Resonance

Quantization of angular momentum

Nuclei

\[ \vec{\mu}_m = \gamma_n \hbar \left[ I(I+1) \right]^{1/2} \]

Nuclear magnetic moments can interact with an external magnetic field

Torque = \( \tau = \vec{\mu}_m \times \vec{H} \)
Magnetic Resonance
Quantization of angular momentum

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Quantization of angular momentum

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Nuclear magnetic moments can interact with an external magnetic field

Torque = \( \tau = \vec{\mu}_m \times \vec{H} \)

Torque induces change in angular momentum

\[ \vec{\mu}_m = \gamma_n \vec{L} \]

\[ \partial \vec{L} \]